Supplementary Information

Photopatterning of ultrathin electrochemiluminescent redox hydrogel films

Materials. Poly(ethylene glycol) diacrylate (PEGDA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), sodium phosphate dibasic heptahydrate, sodium phosphate monobasic monohydrate and tri-n-propylamine were purchased from Sigma. The synthesis of [poly(4-vinylpyridine)Ru(2,2'-bipyridine)$_2$Cl$^-$]$^{+/2+}$ has been reported previously.[1]

Apparatus. Spin-coating was performed using a Caframo BDC6015-220 apparatus. UV light illumination for the photodeposition step was done with a X-Cite 120 lamp. All electrochemical and ECL experiments were performed with a μ-Autolab Type III electrochemical station. ECL intensity was measured using Hamamatsu photomultiplier tube R4632 while ECL spectra were performed by Princeton Instruments spectrograph SpectraPro 2300i. Imaging instrumentation was an epifluorescence microscope Olympus BXFM-ILHSPU equipped with a Hamamatsu CCD camera. All Atomic Force Microscopy observations were recorded using a Veeco Nanosope Multimode 8.

Photopolymer solution preparation. Photopolymer solution consists of poly(ethyleneglycol) diacrylate (PEGDA), 2,2'-dimethoxy-2-phenyl-acetophenone and [poly(4-vinylpyridine)-Ru(2,2'-bipyridine)$_2$Cl$^-$]$^{+/2+}$. First, PEGDA and DMPA were mixed in desired ratio and then this solution was mixed with 5 mg/ml water solution of [poly(4-vinylpyridine)-Ru(2,2'-bipyridine)$_2$Cl-ethylamine in volume ratio 1:1. All solutions were freshly prepared and protected from the light. In the first trials, parameters such as PEGDA/DMPA ratio, dilution factor and illumination time were studied. Different mass ratio of PEGDA/DMPA were tested from 200:1 to 15:1. The 100:1 ratio leads to the highest ECL intensity and it was used in all further experiments. By varying the dilution of the photopolymer solution, we obtained the highest ECL signal by diluting it by a factor 2. The illumination time was also varied from 1 s to 10 s. We selected an illumination time of 5 s because it leads to a fully-polymerised layer with strong ECL signal. Shorter illumination times lead to partially-polymerised film which was not stable on the electrode surface.

Preparation of Electrodes. We used GC disc electrodes, gold disc electrodes and gold coated plates. All disc electrodes were polished using 0.05 μm alumina powder, rinsed and sonicated in Milli-Q water for 2 minutes before use. Gold plate electrodes were cleaned with freshly prepared Piranha solution for 2 hours, then extensively rinsed with Milli-Q water and dried with compressed air just before using. (Caution: Piranha solution H_2SO_4 (98%)/H_2O_2 (30%) = 4/1 must be handled with care.)

Photodeposition and Photopatterning. Freshly prepared photopolymer solution was dropped on the electrode surface and spin coated during 20 s with different rotational speed from 2000 to 10000 rpm. The electrodes are then rapidly placed in front of UV light during 5 sec (Fig. S1). The distanced from the light source was 6.5 cm. By this way we obtained smooth thin films of photopolymer. By modifying the rotational speed we were able to tune the thickness of the photodeposited layers. The procedure for photopatterning was the same with addition of photolithography mask placed 1 mm above the electrode surface. After the UV exposure electrode surface was abundantly rinsed with Milli-Q water to remove the part of the photopolymer which was in the shadow part of the mask and remained non-polymerised during the process. Obtained photopatterns were dried and kept at the ambient temperature.

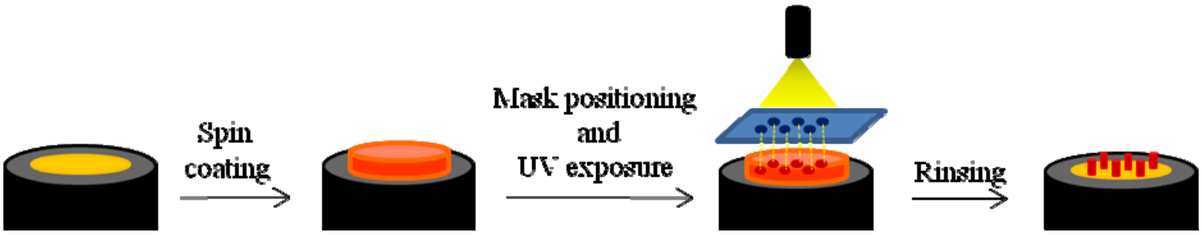

Fig. S1 Scheme of photopatterning procedure to obtain spots of ultrathin ECL hydrogel film.

Electrochemical and ECL experiments. Photopolymer modified electrodes were characterised by cyclic voltammetry. A three-electrode electrochemical cell was used with a Ag/AgCl/KCl electrode, a Pt wire and the modified electrode as reference electrode, counter-electrode and working electrode, respectively. For ECL experiments a special home-made three-electrode cell was used. The cell was placed in front of a photomultiplier tube (PMT) operating at 1000V with 5 mm of total distance between electrode surface and optical window of PMT. All experimental set-up was placed in dark box. Spectra were registered during a constant potential step of + 1.05 V. For comparison, another GC was modified by electrodeposition of $[\text{poly(4-vinylpyridine)-Ru(2,2'-bipyridine)}_2\text{Cl}^-]^{+/2+}$ and ECL spectrum was recorded in the same conditions. Fig. S2 shows both ECL spectra obtained for electrode modified by photodeposition and electrode modified by electrodeposition. It can be observed that spectra are identical indicating that there is no change in complex structure due to entrapment in PEGDA hydrogel.

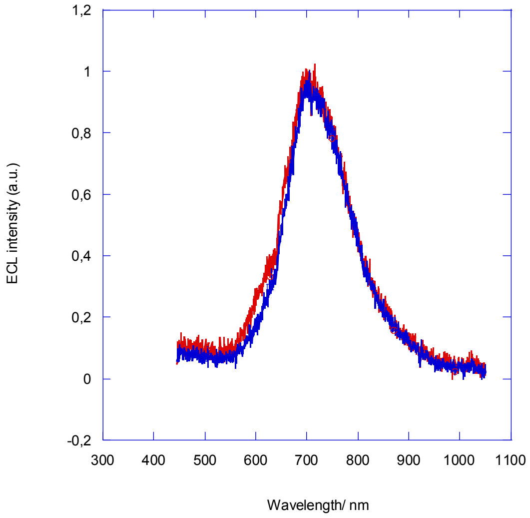

Fig. S2 ECL spectra of photodeposited film (red) and electrodeposited film (blue) on GC electrode obtained in 10 mM TPrA solution. pH = 7.4

References

1. S. Sallard, J. Patole, V. Soukharev, A. Heller, N. Mano and N. Sojic, *Electrochemistry Communications*, 2009, 11, 599.